ON THE EXPERIMENTAL EVIDENCE OF THE MOSAIC STRUCTURE OF BI SINGLE-CRYSTALS

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It is known that the description of the structure of a normal crystal as given by the theory of the atomic and molecular lattices is not complete without taking into account a certain kind of irregularities, the presence of which is dependent on the imperfection of the crystal. Thus the conception of the mosaic crystal rose, first given by Ewald and Smekal and others. In two recent papers, Zwicky[1,2] gave theoretical reasons for the assumption that the mosaic structure in a crystal is a regular one, its period depending on the character of the substance and the lattice. Thus, he obtains the aspect that a crystal has a definite structure—a kind of a secondary lattice—superposed to the molecular or atomic arrangement in the primary lattice.

The experimental facts previously known which can be interpreted in favor of this theory are not very many, and of a more or less indirect kind and mostly taken from non-metallic substances. There are only two phenomena known which may count as visible evidences of the mosaic structure. One is observed by Wood[10] on potassium chlorate crystals, explained by him as a periodical occurrence of twinning, the other concerns ultra-microscopic observations by Traube[3] of the "submicronic" state of crystals of very complex molecules during the act of solution into an almost saturated solvent. The fact that a crystal dissolves first into a large number of particles being within the visibility of an ultra-microscope before being dissolved in molecular dispersions, may be due to the presence of a mosaic block-structure.

The following is a partial report of observations of two different kinds, one dealing with microscopic measurements on Bi single-crystals, the other concerning a study of the conditions in which the orientation and perfection of a growing crystal can be predetermined by inoculation with a seed-crystal. Inasmuch as the ways in which these measurements were obtained differ considerably, the reports shall be published separately. The present paper deals with the microscopic investigation.

The material for the observations were Bi single-crystals grown by a special method (which is to be published soon) allowing one to grow metal crystals of lengths of 200–300 mm. and diameters of 2–7 mm. in *any desired orientation.* It seems necessary to emphasize this last fact for the reason that previous authors (Bridgman,[4] Tyndall,[5] Kapitza,[6] *et al*) had difficulties in growing crystals of all orientation in one and the same apparatus under the same thermal conditions. The fact that it was possible by this method to grow crystals of any desired orientation shows that the method of production does not apply influential forces to the growing crystal, forces of a kind as were experienced by Kapitza (loc. cit.), Hasler[7] and the author and which will soon be discussed more extensively in another paper.

It is well known that the Bi crystal crystallizes in a hexagonal system with a rhombohedral symmetry which approaches almost a cubic one. The plane normal to the trigonal axis is a perfect cleavage plane (111) through which three other imperfect cleavage planes $(11\bar{1})$ intersect, thus forming a pseudo-octahedron. Furthermore, it is known from the measurements of Mügge[8] that any plastic deformation in a Bi crystal results in twinning along the (110) planes where the perfect cleavage interchanges its orientation with an imperfect one, due to the fact that the energy levels of both are almost the same.

With regard to the immediate occurrence* of twinning at the slightest mechanical stress applied to a crystal at normal temperatures, it is easily explainable that one observes under the microscope with small magnification (10–40$\times$) three sets of lines crossing the main cleavage plane and intersecting each other at an angle of 60°. This observation already described by Kapitza[6] makes it easy to distinguish between the perfect and imperfect cleavage planes. Etching shows that these twin lamallae, i.e., their $(11\bar{1})$ planes, are much faster attacked by the acid than the (111) plane. Figure 1 shows the view of a slightly etched main cleavage plane which was plastically deformed, thus showing the occurrence of two different sets of twin lamellae.

If one looks at a perfect cleavage plane with a small magnification one observes besides the lamellae a formation as shown in figure 2 consisting of very irregular black regions and an innumerable amount of small curved lines. Closer investigation shows, that a cleavage on Bi never being exactly parallel to the cleavage plane, cuts a large number of layers which are distinctly separated. The irregular lines are the edges of different (111) lamellae cut in various directions, whereas the large black regions are shadows, cast by protruding edges. It is very remarkable that the cohesion of a Bi crystal parallel to the main cleavage plane is so small that one gets the impression of cutting through a parcel of very thin foils. Figure 3 shows a larger magnification of a more careful cleavage. Although the object is not etched, one can easily recognize the twinning lamella with its peculiar structure, whereas the indistorted regions show the foil-like structure of a (111) plane.

Searching for a microscopic criterium of the perfection of crystals produced by different methods, we † found that if we applied high-powered objectives (oil immersions) to a region of a very good unetched *fresh* (111) plane which was not intersected by any twinning lamella, we could observe

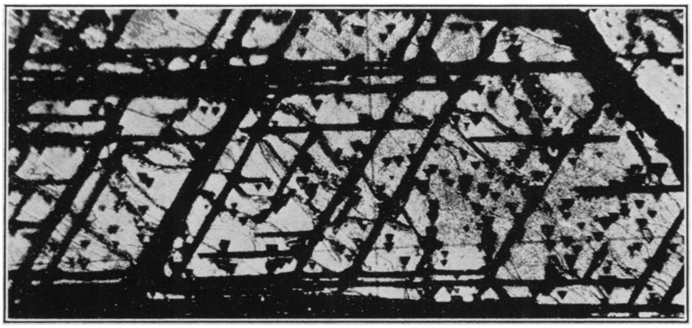

FIGURE 1

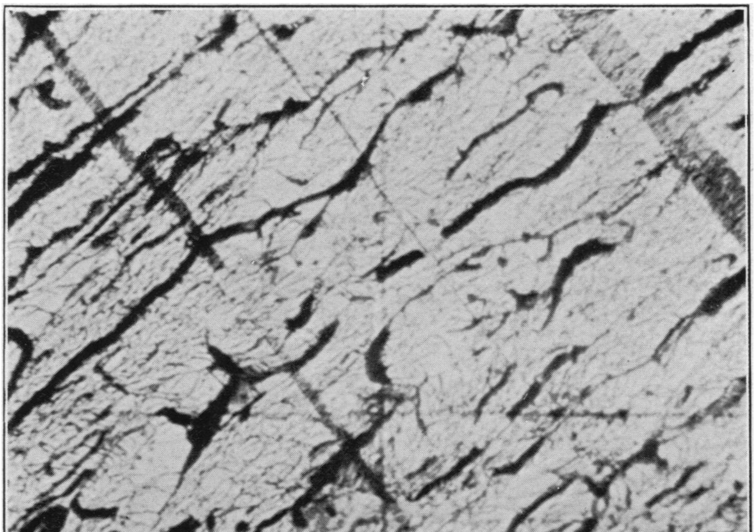

FIGURE 2

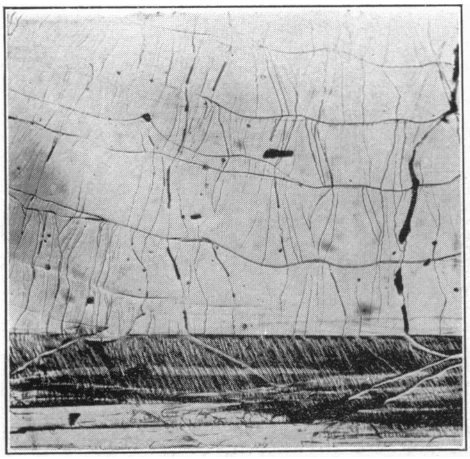

FIGURE 3

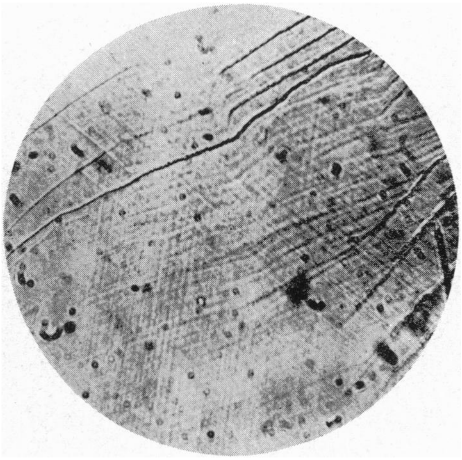

FIGURE 4

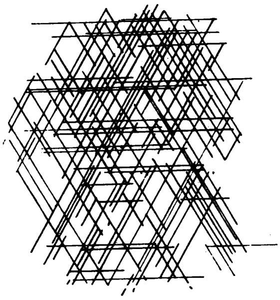

FIGURE 5

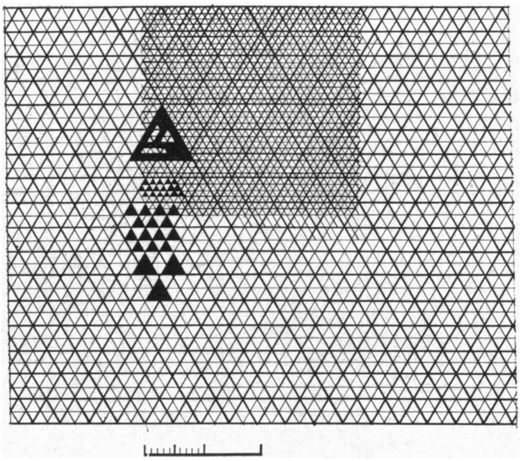

FIGURE 6

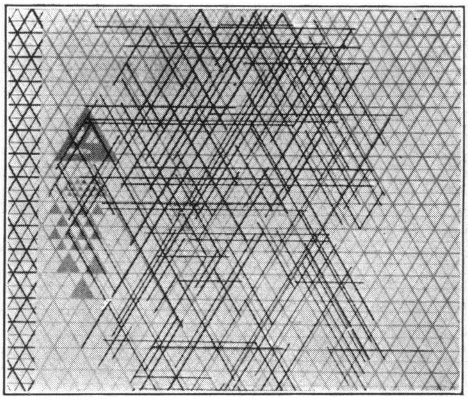

FIGURE 7

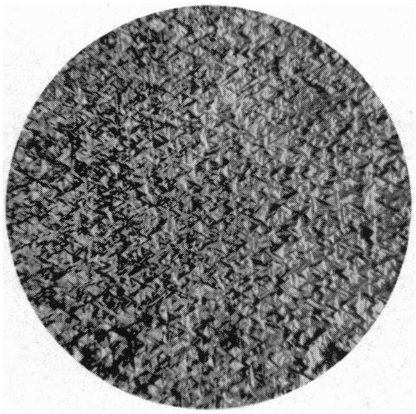

FIGURE 8

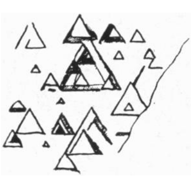

FIGURE 10

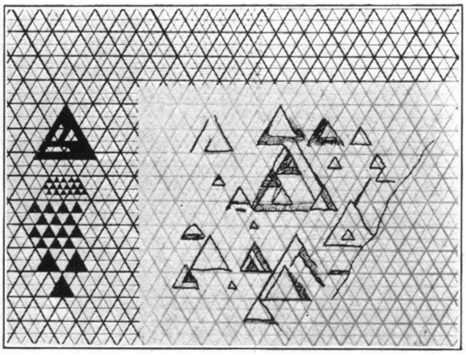

FIGURE 11

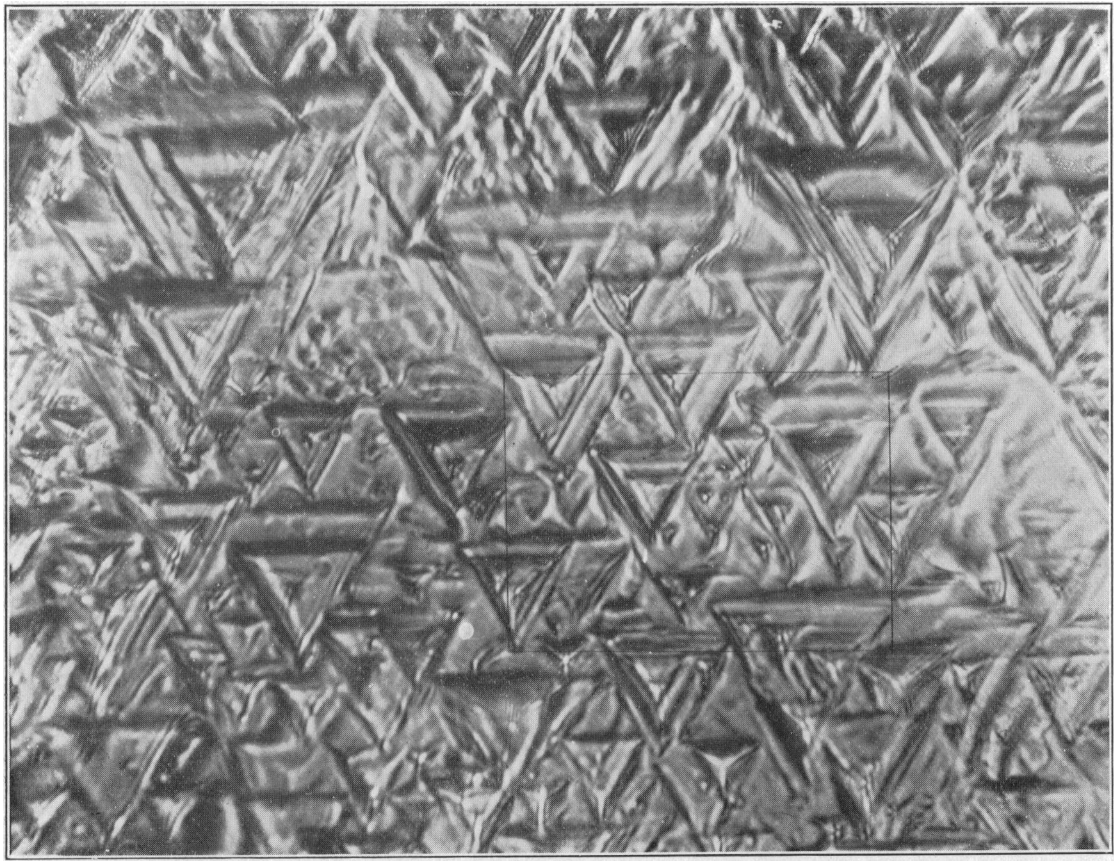

FIGURE 9

a very faint but distinctly visible pattern of lines which cross the whole field of vision. Those sets intersect each other at 60° and run parallel to the twin-lamella (in case those are perfect enough to run straight). The striking feature of these lines was their perfect equidistant occurrence which distinguishes them from the more or less rough twin lamellae.

The objective which gave the best observations was a short mount apochromatic oil immersion (Leitz) (f = 2mm.) (n.a. = 1.4) used with a Beck-Illuminator, having, for green light, a resulting resolving power of 2000 Å. The fact that the pattern appears to consist of very thin lines, the width of which is below the resolving power, makes it only possible to photograph the pattern of the shadows they cast as soon as the illumination is a trifle out of center. This can be obtained easily by bringing the microscope slightly out of focus (ca. 0.3 micron) which destroys the sharpness of the pattern but increases the contrasts so that a photograph can be taken. Although all the appliable photographic tricks were used to make the pattern more contrasting, no better success than the picture in figure 4 could be obtained.

Hence it was necessary to think of another method of reproducing and measuring the regularity and the size of the pattern to find whether or not the distances of its lines proved to be a whole-number multiple of an elementary distance. The only way to do it was by direct vision, because it was found that an especially trained eye after a sufficient time of accommodation is able to record extremely small differences in contrast. After some experimenting, it proved possible to see most of the lines when the objective was in focus. To record the lines correctly, an Abbé-drawing-apparatus was used, which allows one to bring the drawing in a direct optical relation with the original. The fainter the lines, the more regular they were, so it was sometimes necessary to bring the objective slightly out of focus, first in one direction, then in the other, thus casting faint shadows to the two sides of one line, and to mark with an artificially illuminated pencil-tip the border they had in common. Thus drawings of the type of figure 5 were obtained.

Several kinds of Bi were tried of different degrees of chemical purity and different crystalline perfection. It was found generally that *the smallest distance of the triangular pattern* over an undisturbed area on the main cleavage plane *was the same* within the limits of error, which error was estimated at not possibly more than 20% of the whole.

For measuring this distance and deciding about the existence of an integral-number-arrangement, the following method was used: The measured smallest distances were averaged and a pattern of equal sided triangles was drawn (Fig. 6) and then projected into the microscopic field of vision by means of the drawing apparatus, so that the lines of the constructed pattern fitted the visible lines on the crystal. It was observed that if the parameter of the drawing was not exactly the same as in the specimen, the eye could separate easily the two superposed images. Finally, it was possible to obtain one drawing which disappeared almost entirely in the pattern of the specimen, thus showing that the right parameter had been obtained quite correctly. Then the crystal under the microscope was replaced by a steel-engraved micrometer of 10^{-3} cm. distance, for the calibration of the drawing. The length of the basal side of the smallest triangle was measured to be 1, 4 .10^{-3} mm. $\pm$ 0.2 μ.

The drawn copies of the visible pattern made on transparent paper were then superimposed onto the constructed pattern as shown in figure 7 and it became evident from all obtained drawings that the visible pattern was a fragment of a pattern which fitted the constructed one, i.e., *no line was found which did not fit a line in the constructed drawing even though if not visibly connected to the coherent part of the observed pattern.* The fact that it was never possible to see the whole pattern, the constructed drawing called for, finds its explanation in the unavoidable imperfection of a cleaved plane of a soft metal; whereas the fact that there was never a line observed where there was none predicted by the drawing, leads to the conclusion that *the distances of the observed lines are whole-number multiples of a smallest-occurring unit of the stated size,* which unit is independent of the perfection, the purity, and the individuality of the Bi crystal. The question, if these observations are not due to an optical delusion caused by the resolving limit of the objective, can be answered in the negative, since the smallest resolved distance in the used arrangement is 5–6 times smaller than the size of the triangles. The power of the eyepiece was always small enough to obtain a sufficient field of vision, but large enough to separate by eye, within the distance of two elementary lines, 4 to 5 pencil lines in the projection of the drawing on the subject.

Another evidence that these triangular cells have individual qualities was derived from the etching figures obtained on these (111) planes. The etching medium giving the best pattern was found after some experimenting to be nitric acid (C. P.) diluted in distilled water (1:3) at ca. 25°. The acid has to contain a sufficient amount of bismuth nitrate to increase the speed of etching. The plane has to be cleaved just before the acid is applied. After 30 to 60 sec. the acid has to be rinsed off by warm distilled water, used for dissolving completely the traces of Bi $(NO_3)_3$ formed on the plane. The specimen should be protected after drying with a drop of immersion oil to prevent oxidation. Hence it is possible to obtain after some experience a pattern of the type shown in figure 8 giving the impression that the former plane is changed into a field of an innumerable amount of triangular pyramids of different sizes. Larger magnifications reveal that the pyramidal holes have steps of a very regular size, also that the smallest pyramids have the most perfect symmetry. The size of the average pyra-

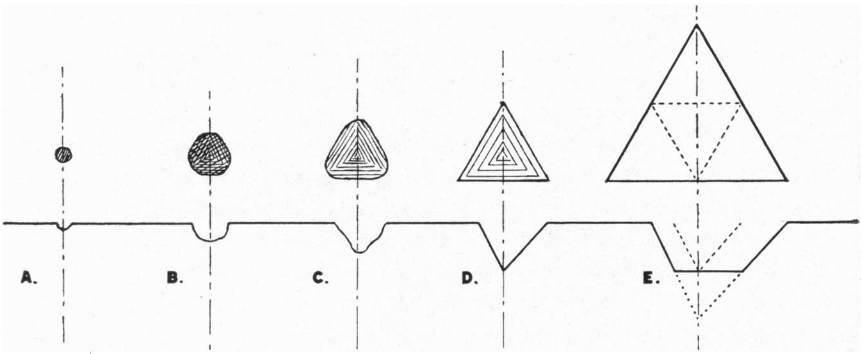

FIGURE 12


FIGURE 13

mid obtained by etching depends very much on the cleanliness of the surface, the temperature, the concentration of the acid, etc. Under the given condition (etching immediately after cleaving), the size of the pyramids is rather uniform. It was found that the size as well as the degree of uniformity depends on the time of etching. The optimum is reached in general with the time mentioned above.

A plane thus etched permits one to use large magnifications and to make a close investigation of the nature of the pyramids and of their size. (Fig. 9.)

Determining thus the qualities of the pyramids on several hundred different crystals, it was found that *there exists a "smallest" pyramid, its length of the basal plane on each side being 1.4 ± 0.2 micron, which,* within the limits of the obtained accuracy, *is the same as the size of the triangles on the unetched plane.* Furthermore, the identity of the pattern on the unetched plane and the location of the etching figure could be proved by means of making drawings first of the fresh plane (Fig. 5) and later after etching of the same region. Figure 10 shows a drawing of the etching figure and figure 11 shows that its superposition on the constructed pattern works as well as in the case of the line pattern. The fact that the etching process changes the aspect of the plane entirely makes it necessary to have an added point of reference to control the position of the object in spite of the high precision of the used mechanical device. A very small twin lamella within the microscopic field of vision fulfills this purpose admirably because of the difference of its etching pattern. Thus it could be shown that the outline of a triange after etching became the border of a pyramid, i.e., *the location of the etching pattern was predetermined by some kind of periodic inhomogeneity within the crystal.*

Special attention was paid to the study of the different phases in the genesis of the smallest etching pattern. The process in different states is shown in figure 12, which is a free-hand sketch. The dissolving process starts (in case the region of the plane is perfect) at a point which is always within the borders of a triangle, never across one line. The groove is generally round (Fig. 12 A) when its size is above the resolving power of the objective and it continues to grow in a round shape (Fig. 12 B) until it comes close to the sides of the triangle. There the dissolving process stops (Fig. 12 C) and proceeds into the corners of the triangle until a sharp-cut pyramidal pattern is reached (Fig. 12 D). If the acid is not removed at this moment, the borders of this triangle are crossed and then four pyramids unite to form one large hole (Fig. 12 E). Still later, four of these larger pyramids join, etc. But the regularity of the union of large numbers of pyramids is seldom perfect, apparently because there is only a small probability that the same surface conditions hold over larger areas.

Figure 13 shows a region indicated on figure 9 under a still larger magnification for the demonstration of the different phases of the formation of the smallest pyramids.

The conclusion which can be drawn from these observations is that *the chemical affinity inside one block is larger in its center and considerably smaller at its borders,* which agrees very well with the prediction drawn from the theoretical aspect given by Zwicky.[2]

The fact that the side planes of the pyramids being apparently parallel to the $(11\bar{1})$ planes can form protective walls against the chemical dissolution is not in agreement with the fact that the atomic distance within these planes—as is given by Bragg diagrams—is larger than in the (111) planes (James [9]) which should result in a larger chemical affinity. The theory of Zwicky postulates that the separating walls of the "blocks" are of a higher density than indicated by the x-ray diagram, so that it is possible that the affinity of a $(11\bar{1})$ plane in the contracted state can be actually smaller than of a (111) plane.

Moreover, the same is true for the border planes of the blocks parallel to the (111) plane, which are visibly evident by the step-structure of the pyramids. Unfortunately, it is very difficult to obtain good measurements along the direction of the optical axis of the microscope at very large magnifications, hence it is not possible to make reliable statements about the depth of the steps. It must be approximately 1 micron, i.e., smaller than the basal length (Fig. 12, D and E).

The fact that the cohesive forces normal to the (111) at room temperature are very small compared with the forces in any other direction of the crystal induces the assumption, that the blocks could be easily separated parallel to this plane. One observes indeed on each cleavage along a (111) plane as mentioned above, that it cuts a large number of steps (Fig. 1). If the cleavage is done with caution, the height of these steps is very small and there is evidence that this height is the same for all of them or a whole-number-multiple and *is identical with the depth of the steps in the etched pyramids.*

Summary.—The described microscopic observations seem to lead to the conclusion that a Bi crystal consists of "blocks" of a definite size, which size is independent of the perfection of the crystal, as long as the crystal is not plastically deformed. When a deformation causes a twinning, the thickness of the smallest twin lamella is approximately the size of one "block."

The observations follow qualitatively the predictions made by the theory of Zwicky; the fact that the parameter of the "blocks" is 40% larger than the maximum given in his paper does not mean necessarily a disagreement because no quantitative statement can be made as long as the value of the Poisson number of Bi crystals is not known.

It could not be decided whether or not the described "block" is the small-

est unit of a crystal above the lattice unit. However, the existence of a smaller unit seems to be improbable for the reason that although the measured unit is 5 times above the resolving power, smaller units of the whole-number-multiple pattern could not be found, as one should expect in case of the existence of a submicroscopic unit.

Nothing can yet be said about the constitution of these "blocks" because it is impossible to investigate the nature of the lines, but it is very probable that these lines indicate regions of larger density, as indicated by their chemical behavior.

This makes us think of a "block" as an ideal crystal surrounded on all sides by a very thin hull of higher density. With regard to this structure, it is easy to identify the fissures parallel to the (111) plane in Bi crystals, indicated by the experiments of Kapitza.[6] He found that the variations of the specific resistance parallel to the trigonal axis of Bi crystals disappeared and approached the normal value as soon as he applied a pressure to the crystal in the direction of the current. There is little doubt that these fissures are caused by the above-mentioned extremely small cohesion parallel to the (111) plane along the borders of the "blocks."

I feel very much indebted to Dr. F. Zwicky for many theoretical suggestions which stimulated the investigations in this special line. Moreover, I should like to express my appreciation of the assistance given by Mr. M. F. Hasler and Mr. A. B. Focke.

* This is probably only true in the case of very pure metal and perfect single crystals.

† The discovery of this phenomenon was made practically simultaneously on the same object by Mr. Hasler, Dr. Zwicky and the author.

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[2] F. Zwicky, *Ibid.*, **15**, 816 (1929).

[3] J. Traube and W. von Behren, *Zeit. Phys. Chem.*, **138A**, 85 ff. (1928).

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[5] A. G. Hoyem and Tyndall, *Phys. Rev.*, **33**, 81 (1929).

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[10] R. W. Wood, *Physical Optics*, p. 160 (1911).